Title: Influence of substitution of the chromium ions by the nonmagnetic Sb and Al ions on the magnetization processes in CuCr2X4 (X = S, Se) spinels

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Influence of Substitution of the Chromium Ions by the Nonmagnetic Sb and Al Ions on the Magnetization Processes in $CuCr_2X_4$ (X = S, Se) Spinels

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Both the dc and ac magnetic susceptibilities as well as magnetization measurements were used to study the influence of the dilution of the magnetic chromium subarray by nonmagnetic antimony and aluminium ions on the magnetization processes for four spinel families under investigation. Substitution of the chromium ions by the nonmagnetic Sb and Al ions in the compounds under study leads to the very hard magnetization in the case of the compounds with Sb and very easy magnetization in the compounds with Al. This effect is connected with the electronic configurations of the Sb and Al ions as well as with ionic radii of these cations.

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1. Introduction

Spinel matrices $CuCr_2S_4$ and $CuCr_2Se_4$ mentioned in the title of this abstract are strong ferromagnets with the *p*-type metallic conductivity. For both these compounds the Curie temperatures T_C as well as the Curie–Weiss temperatures θ_{CW} are of the order of 500 K. On the base of these matrices four spinel families were obtained via substitution in the B-sites of the magnetic chromium ions by the nonmagnetic Sb or Al ions. Three of these families turned out to be stoichiometric: $CuCr_{2-x}Sb_xS_4$ (x = 0.3, 0.4, 0.5) [1], $CuCr_{2-x}Sb_xSe_4$ (x = 0.1, 0.2, 0.5, 0.8, 1.0) [2], $CuCr_{2-x}Al_xSe_4$ (x = 0.1, 0.2, 0.3, 0.4, 0.5) whereas the fourth one, namely: $Cu_{1+x}Cr_{1.5+y}Sb_{0.5+z}Se_{4+t}$ (where $-0.02 \leq x \leq 0.01$, $0.03 \leq y \leq 0.35$, $-0.2 \leq z \leq -0.02$, $0.01 \leq t \leq 0.08$) [3] occurred to be nonstoichiometric. All powder samples mentioned above were obtained by ceramic method. The chemical composition of the samples was determined with the aid of the atomic emission spectrometry. For this purpose a method of the inductionally coupled high frequency plasma (ICP-AES) was used. The aim of this paper is to show the influence of the substitution of the magnetic chromium ions by the nonmagnetic Sb as well as Al ions on the magnetization processes in the compounds under study.

2. Experimental

The lattice parameters were determined by X-ray diffraction with the use of the SIEMENS D5000 diffractometer. The experimental data were analyzed with the aid of the programs HX61 and Checkceel. The magnetization was measured with the use of the induction magnetometer in the high stationary magnetic fields up to 14 T. Both the dc and ac method were used for the magnetic susceptibility measurements. The dc measurements were carried out with the aid of the Cahn magnetic balance whereas the ac measurements were carried out with the use of the Lake Shore magnetometer.

3. Results and discussion

The above mentioned measurements revealed the appearance of the spin-glass states in all the compounds under study for which magnetic chromium subarray is diluted by nonmagnetic antimony ions [1–3]. Moreover, both the stoichiometric compounds with sulfur anion and the nonstoichiometric ones with the selenium anion magnetize very hard. In spite of the external magnetic field applied up to 14 T the samples belonging to these two spinel families are still far from magnetic saturation. The lack of the magnetic saturation as well as the change of the slope of the rectilinear segments in the magnetization isotherms testify to that in all these samples magnetic spin-flop phase transitions take place (see Fig. 1). As concerns the stoichiometric antimony compounds with the selenium anions, only the sample containing the antimony concentration x equal to 0.1 reaches the magnetic saturation. With the increase of the Sb concentration x the magnetization decreases very fast and the magnetization processes become more and more hard (see Fig. 2). Moreover, the magnetization isotherms exhibit the hysteresis phenomena and very large paraprocesses [2].

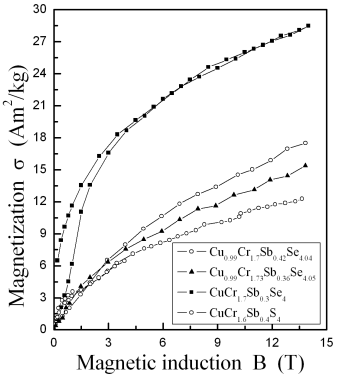

Fig. 1. The magnetization isotherms at 4.2 K of $CuCr_{2-x}Sb_xSe_4$ spinel system and $CuCr_{1.6}Sb_{0.4}S_4$.

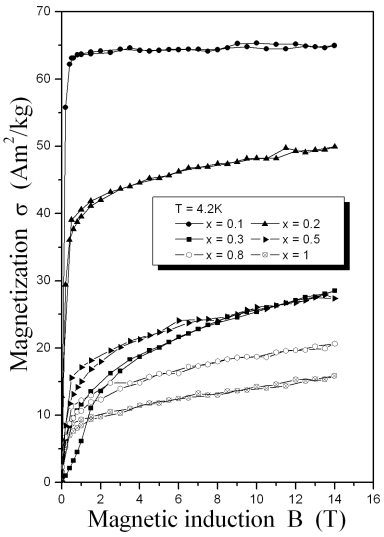

Fig. 2. The magnetization σ isotherms at 4.2 K for the compounds with the general formula $CuCr_{2-x}Sb_xSe_4$ [2].

On the other hand, all the samples containing Al magnetize very easily and reach the magnetization saturation at very low magnetic field (see Fig. 3). To explain the magnetic behavior of the compounds described above one has to take into account both the electronic configuration and ionic radii of Sb and Al cations. Electronic configuration of the Sb^{3+} ions can be expressed as $[Kr]3d^{10}5s^2$. Such configuration causes that ionic radius of Sb^{3+} is large and equal to 72 pm both in the octahedral and tetrahedral coordination.

On the other hand, the electronic configuration of an Al^{3+} ion has the form $1s^22s^22p^6$ which means that the ionic radius of Al^{3+} is small, e.g. is equal to 53.5 pm for the octahedral coordination. Moreover, for the tetrahedral coordination it is very small and equal to 39 pm. Let us note that the ionic radius of Cr^{3+} ion for the octahedral coordination is equal to 61.5 pm.

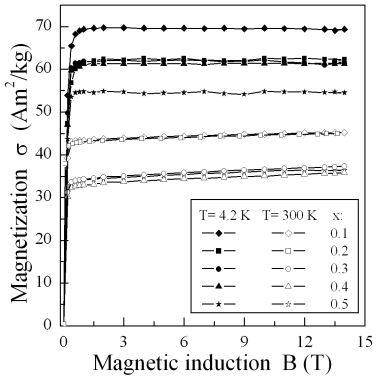

Fig. 3. The magnetization isotherms both at 4.2 K and at 300 K for the compounds with the general formula $CuCr_{2-x}Al_xSe_4$.

Substitution of chromium ions by the nonmagnetic antimony ions, whose radius is much greater than the Cr^{3+} ion radius, causes the break of the paths of both superexchange and double exchange magnetic interactions and simultaneously the increase of the distances between the magnetic ions. Both these factors decrease the ferromagnetic component and increase the antiferromagnetic component. It causes the hard magnetization of the sample with antimony and the rapid decrease of the magnetic moment with the increase of the antimony concentration in the sample (see Fig. 2). The effect described above is particularly well seen for the samples with sulphur anions (see Fig. 1). On the other hand, the substitution of chromium ions by the aluminium ions causes both the break of the paths of magnetic interactions and the decrease of the distances between the ions interacting magnetically. It means that there appears an increase of the ferromagnetic component of the magnetic interactions and the samples reach the magnetic saturation very easily as seen in Fig. 3.

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